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Electrical Detection Problems in Water Analysis by Spark Source Mass Spectrometry

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ELECTRICAL DETECTION PROBLEMS IN WATER ANALYSIS BY SPARK SOURCE MASS SPECTROMETRY

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure specific pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Analytical Chemistry Branch develops and assesses new techniques for identifying and measuring chemical constituents of water and soil.

Spark source mass spectrometry, a technique that has recently been applied to the elemental analysis of water and sediments, meets many of the analytical chemist's requirements for a method that quickly and accurately identifies trace elements in environmental samples. The research reported here describes the development of control features to make the analytical technique more quantitative and easier to use.

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ABSTRACT

This report describes research on factors affecting accuracy in spark source mass spectrometry (SSMS), and the application of SSMS to water-related problems.

This project has also involved the development of instrumental additions to improve the operation and control of SSMS procedures, particularly with respect to making the technique more quantitative and easier to use. The application of SSMS to specific sample types is also demonstrated.

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SECTION I

INTRODUCTION

An increased recognition of the role of trace elements in plant life,[1] animals,[2] the human body[3,4] industrial products[5,6] and processes,[7] etc. has made the scientific community, as well as the general public, more aware of the need to have available dependable and comprehensive monitoring techniques to readily determine what inorganics are present in water, either naturally or from industrial or municipal discharge. Many techniques have been applied to water analysis in recent years. Spectrophotometric methods[8,9] are quite sensitive, accurate, and inexpensive, but they are subject to interelement interferences, respond to only one element at a time in their usual practice, and often require considerable premeasurement steps, such as separations. Certain electroanalytical methods, particularly polarography,[10] have reported relatively simple procedures and good sensitivity. However, they are responsive mainly to metals, and not all of those. Flame emission[11] has been used for metal determinations in water, but only a limited number of metals are normally determined. Atomic absorption is sensitive, simple, accurate, and relatively interference free, but it lacks the sensitivity necessary to examine certain elements at very low levels. A single ideal analytical technique to cover all of these needs might (1) be rapid, (2) be extremely sensitive, (3) be accurate, (4) be responsive to all elements, metals, and nonmetals, (5) provide both a qualitative and quantitative analysis for all species simultaneously, (6) require minimal sample preparation, (7) exhibit uniform sensitivity for all elements, (8) be free from interference or matrix effects, and (9) have a simple and convenient data acquisition readout system. Though spark source mass spectrometry does not meet all of these ideal criteria, it in fact does come closer than any other currently available trace analysis method.

Spark source mass spectrometry (SSMS) was developed in the 1960's, largely in industrial laboratories. Hannay and Ahearn[12] at Bell Laboratories did much of the early groundwork; Ahearn[13] has reviewed the technique. Basically, as shown in Figure 1, SSMS utilizes a high voltage spark (5-80KV) to ionize a sample for subsequent separation in tandem electrostatic and magnetic fields, resulting in identification and analysis of the ions on the basis of mass to charge. The energetic ion source provides essentially uniform sensitivity for all elements in a single scan and allows analysis of refractory, nonvolatile materials such as metals and alloys. A mass range of about 6 to 250 is used routinely, covering lithium through uranium and thus effectively encompassing the entire elemental range. Sensitivities to 1ppb are obtainable, and all elements are detectable at sub-ppm. Serious interferences are few because of the polyisotopic nature of most elements, and matrix has been shown to have relatively little effect on elemental sensitivities. Qualitative and quantitative results for 30 to 50 elements can be obtained. Accuracy of photographic readout is $\pm$ 20% to 30%. Electrical detection allows the more rapid acquisition of data by scanning methods, but accuracy and precision are still in the 20% to 30% range. Peak switch integration methods provide 5% to 10% accuracy.

However, SSMS is not a simple technique. Operator skill and experience are important in obtaining meaningful results. The need for control of experimental variables is recognized. Our research has involved the development of control features to make SSMS more quantitative and easier to use for trace element analysis.

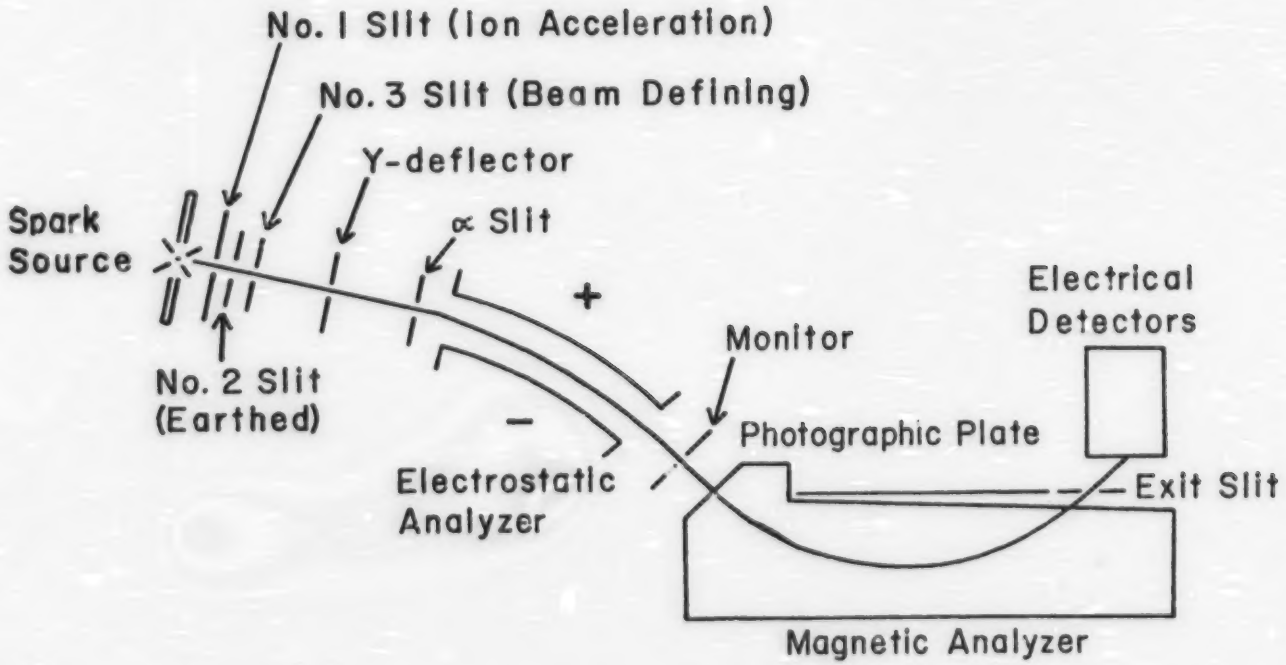

Figure 1. Schematic diagram of MS-702 spark source mass spectrometer.

SECTION II

CONCLUSIONS AND RECOMMENDATIONS

If close attention is paid to experimental variables, spark source mass spectrometry can serve as a complementary technique to other analytical methods for obtaining qualitative and quantitative information concerning trace elements in water and related samples such as sediments and tissues. Control features added to the spectrometer allow these analyses to be performed more conveniently and precisely.

A spark source mass spectrometer is an expensive and complex unit, and thus its widespread use in water analysis is precluded. For large regional, state, or federal laboratories, however, this technique is invaluable for use on materials that require complete elemental screening. A spark source mass spectrometer should be considered for inclusion in such facilities.

SECTION III

EXPERIMENTAL

APPARATUS

The basic AEI MS-702 spark source mass spectrometer and experimental parameters have been previously described.[14] The standard AEI electrical detection systems[15] was added and used for all data in this study. Appropriate magnet current, acceleration voltage, electron multiplier voltage, and sensitivity settings were determined for each isotope measured. Modifications or additions to the standard system include:

A spark gap monitor pickup coil mounted externally in a source port fed an RF voltage to a Tektronix Model R564-B oscilloscope for display.

A modification of a Kennicott telescope mount[16] was used with a 30 x optical system, cross-hairs, and calibrated reticle to carefully align the electrodes on the ion beam axis and to view the discharge during sparking. Rack and pinion focusing of the shallow depth of field optical system allowed measurement of spark-to-No. 1-slit distance on a calibrated scale.

The standard spark shield was modified to provide a light entrance from the top (for the overhead light source) and a 2.5 cm. square front viewing window. The latter allowed full view of both electrode pairs and was covered with a replaceable glass plate held in place by tabs cut into the spark shield.

A continuously variable (0.0.012-inch) V-shaped collector slit was substituted for the standard two-position slit.

The standard AEI source chamber was replaced by a larger unit, designed and constructed in our machine shops to accom-

modate a 1200 liter/sec oil diffusion pump, cold trap-baffle, and gate valve (all from Varian, Vacuum Division, Palo Alto, Calif.). The seldom-used 2000 time constant for magnet scanning was also replaced by a more useful 150 time constant.

A linear ratio output was obtained[17] for peak area comparison by inputting the logarithmic output of the AEI ratio amplifier to an antilog converter consisting of an inverting amplifier (Analog Devices, Model 141C) and a logarithmic function module (Teledyne Philbrick, Model 4350) wired in the antilog configuration. The linear ratio was input to a V-F converter and counter (Heath UDI, Model EU-805) and the output pulses were directed to a 4096 channel MCA (EDAX, Model 706) for spectra accumulation. Each channel of the MCA can accept up to 10^6 counts. A visual readout module (EDAX, Model 871N), which intensified and integrated operator-selected channel bands of the MCA cathode ray tube display, was used to obtain all peak areas. A conventional oscillographic recorder was also available.

ASHING OF BIOLOGICAL TISSUE

The tissue is dried at 105°C in an oven for several hours and preferably overnight. Vacuum drying at 100°C in a "drying pistol" can be used to accelerate the process and also provide protection from contamination. One-gram tissue samples are taken, if available, although samples as small as a few mg have been analyzed. Large tissue sections ($\sim$ 1 g) should be cut with a scalpel into smaller pieces to facilitate both drying and ashing. Plastic or Teflon vials are used for sample storage. Quartz ashing boats are preferred to reduce elemental pickup during HTDA and LTDA. Quartz beakers or flasks are used for wet ashing.

High-Temperature Dry Ashing

The dried tissue is ashed at 550°C in a muffle furnace overnight. The quartz boats in the furnace are protected from any material falling from the walls and ceiling of the furnace by insertion into 1 1/2 inch Pyrex tubes. The ashed residue may be scraped from the quartz boat and mixed directly with 50 mg of graphite. This is transferred to a plastic vial containing a plastic pestle, and shaken for 15 minutes on a Wig-L-Bug to achieve a homogeneous mixture. Alternatively (and the method we prefer), the ash residue is moistened with a few drops of 1:1 HNO_3 and loosened with a spatula. The dissolved-suspended mixture is washed from the boat into a Teflon beaker, the graphite added, mixed to a slurry, and the material dried under an IR lamp. This

residue is then treated on the Wig-L-Bug as above. Two electrodes are tipped out by using the standard AEI Sample moulding disc.

Low-Temperature Dry Ashing

The dried, chopped, tissue is placed in a quartz boat and ashed for several hours (or overnight). The material may require, depending upon effective surface area, turning or breaking up at selected intervals. Hair samples oxidize very readily with no agitation; however, liver tissue may form hard oxide encrusted particles that resist further oxidation unless broken up. The ash residue may be transferred to a plastic vial and homogeneously mixed with graphite in the Wig-L-Bug. For very small samples, a few drops of 1:1 HNO_3 is helpful in collecting the residue, with subsequent wash-transfer into a weighed amount of graphite for drying and homogenization.

Wet Ashing

Although we have used HNO_3-$HClO_4$ wet ashing for the analysis of many biological materials, particularly samples of 50 mg, there are certain hazards which can make a written "standard" procedure dangerous. The solution must be taken to or near dryness to evolve the excess $HClO_4$ and this can cause difficulties if done too rapidly. In general, we try to use one of the dry ashing procedures for all SSMS tissue analyses.

SECTION IV

RESULTS AND DISCUSSION

INSTRUMENTAL DEVELOPMENTS

Spark Gap Control

One of the more difficult parameters to maintain constant is the spark gap between the electrodes. Many investigators make no particular effort to monitor and control the gap. However, it has long been known that interelectrode gap width can be significant. Woolston and Honig[18] demonstrated that the energy distribution of ions in the beam is affected by gap. Bingham and Elliott[15] cited gap effects in high accuracy peak switching analysis, as have Colby and Morrison.[19] Konishi and Nakamura[20] have noted gap effects on ion ratios using photographic detection. This laboratory has also reported effects of gap width on sensitivity[21-23] which showed marked changes in analytical ion yields with changing gap width for aluminum, copper, and steel matrices. More recent work with compacted graphite samples indicates an even greater dependence. The Autospark (A.E.I.), a standard part of the electrial detection system, is useful for maintaining spark ignition, but its cyclical nature continuously varies the interelectrode gap. Manual gap adjustment, as determined by oscilloscopic display of the breakdown voltage, has been our standard procedure in those studies calling for maximum precision, but this is tedious and keeps the operator constantly engaged. To obviate these difficulties, a unit has been designed and constructed in our laboratories which automatically maintains a preselected gap width, correcting for both short term and long term effects of electrode deterioration. The unit described in this paper is specifically designed to coordinate with a commercially available electrial detection package currently in use in many laboratories.

The automatic gap controller utilizes the amplitude of the RF voltage developed between the electrodes as the controlling signal. The amplitude to which the RF builds before breakdown is directly proportional to the spark gap width. Our Automatic Gap Unit (AGU) continuously adjusts one electrode in order to maintain a fixed RF voltage between the electrodes, and thus a constant gap.

The AGU was designed and constructed to be used with an AEI MS-702 spark source mass spectrometer and to utilize certain AEI Autospark components. The entire schematic of the AGU and associated Autospark components is shown in Figure 2.

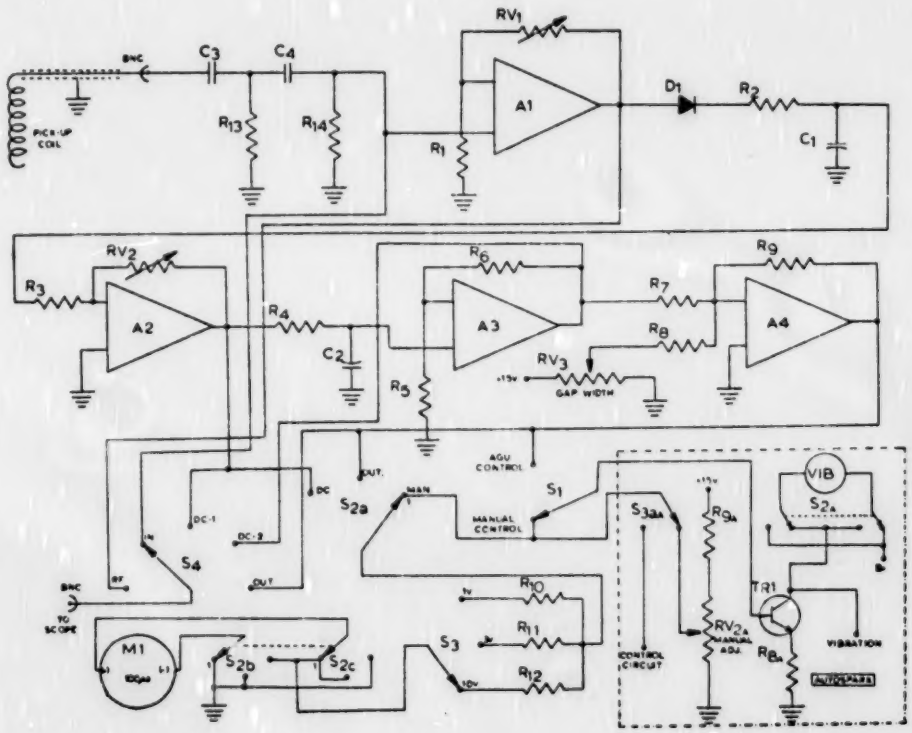

Figure 2. Schematic diagram of automatic gap unit. See reference 22 for details.

The AGU has proved to be extremely useful for a broad range of sample types. It is capable of maintaining a stable gap with close tolerance at widely varying sparking conditions.

Voltage vs. Current Control--

A device to maintain automatically the spark discharge for SSMS may be current or voltage controlled. With the current control mode,[9] the current flowing in the spark circuit is sensed and used as the governing signal while in the voltage type, the RF breakdown voltage between the electrodes acts as the control signal. Figure 3 demonstrates another area in which the AGU has proved to be helpful. The trace shows variations in gap width while sparking a particularly low impurity graphite sample (such as encountered in water analysis). This electrode type often has a tendency to partially fragment, producing small carbon particles which may momentarily short out the electrode gap. The Autospark (first ten minutes of the trace) was unable to keep the spark running continuously without operator intervention. Points (w), (x), (y), and (z) are such points where a manual restart of the spark was required. The carbon fragments drastically disturbed the normal operating rhythm of the Autospark, because it is actuated by current. When the gap is shorted by a carbon fragment, the current drops to zero. The Autospark, however, cannot distinguish this from an open circuit gap, because it too results in zero current. Thus, the Autospark must cycle in order to reinitiate the spark.

The AGU repsonds quickly and properly to the carbon fragment phenomenona, resulting in a minimal amount of off-time. This is shown in the last eight minutes of the scan in Figure 3. When the gap is shorted by a fragment, the voltage between the electrodes decreases (a), but this drop is unambiguously interpreted as an electrode short, thus calling for a electrode separation. The controlled electrode backs off and the fragment is ejected from the gap, leaving the inter-electrode distance too large. This results in a momentary increase in RF (b) above the present level. The AGU also senses this and rapidly decreases the gap width to the desired maintenance level.

Need for Gap Control--The effects which may be produced by a variation in gap width point to the need for rigid spark gap control. This is illustrated in Figure 4 where the cyclical nature of the Autospark is again evident. Each point

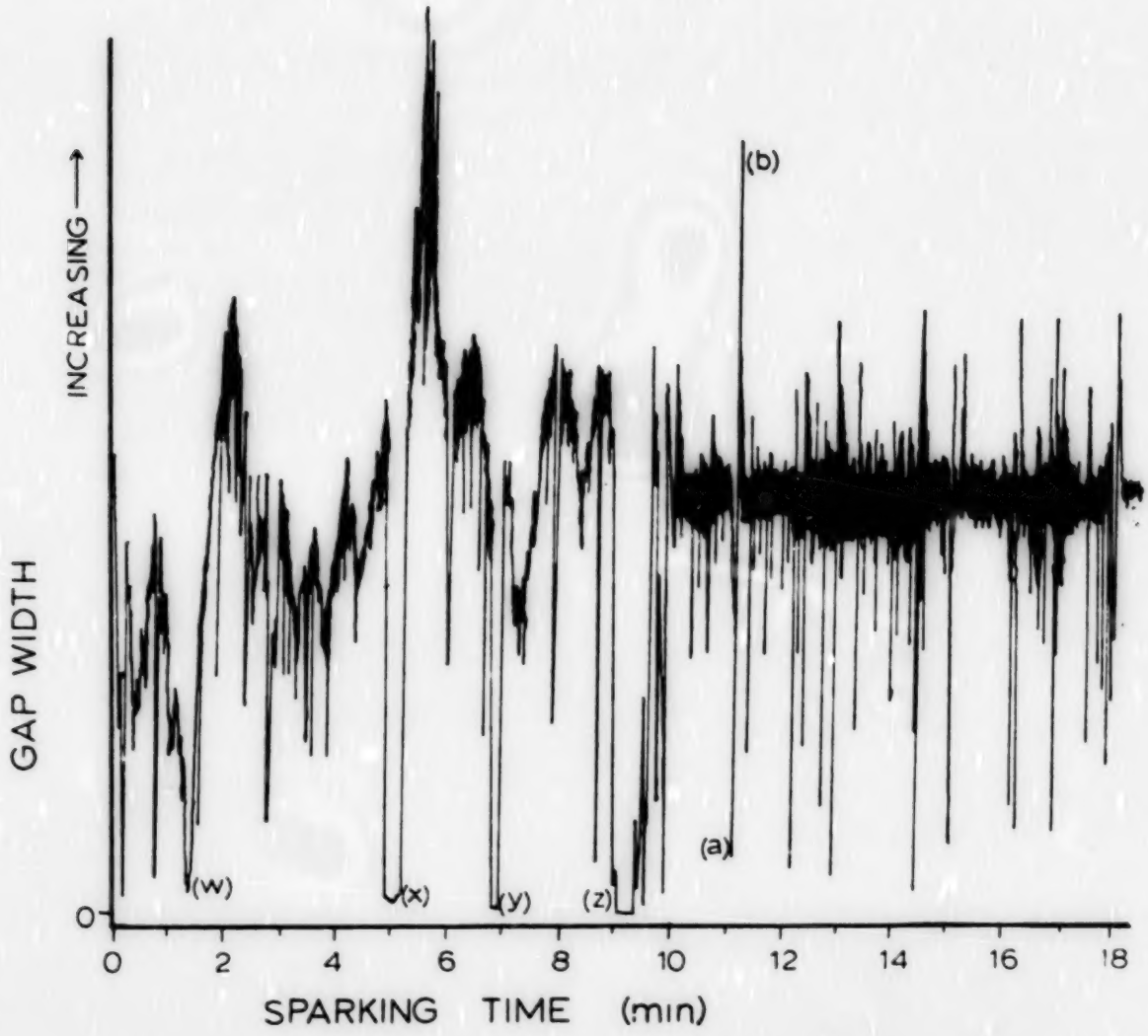

Figure 3. Gap width stability comparing the Autospark and AGU (poorly sparking compacted sample). Points (w), (x), (y), and (z) are where manual re-initiation of the spark was required. (a) Momentary narrow gap; (b) momentary wide gap. Moderate vibration used throughout.

in the two plots, offset from each other for clarity of graphing, is an integration of the analyte ion ($^{39}K^{+1}$) for a total ion beam charge accumulation of 0.1 nC. These were taken every ten seconds to show how the effects of gap width can be transmitted to the final data. The relative standard deviation for the points in plot (a) is $\pm$ 8.9%, as opposed to $\pm$ 2.1% for those of plot (b). Techniques and instrumentation in SSMS are now to the point where gap effects of this magnitude may contribute significantly to the overall precision and accuracy of an analysis. Through very careful sample preparation, precisions from 5 to 12%[24] on compacted samples are possible, even utilizing photographic detection. In peak switching electrical analysis, with precision of better than 2% possible, stringent gap control is in order.

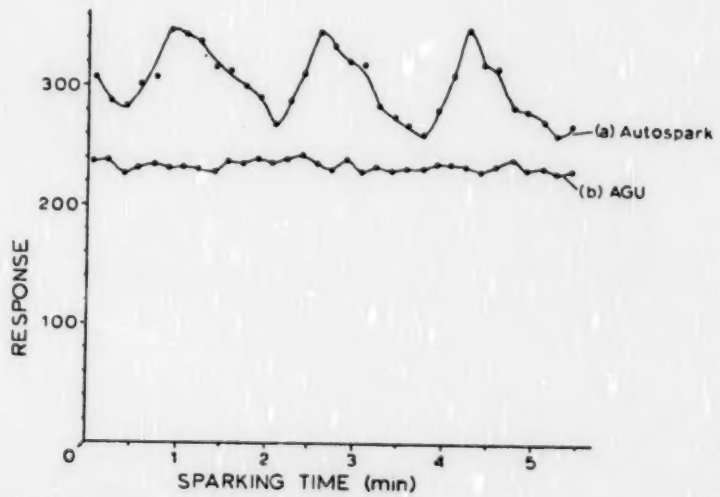

Figure 4. Effect of gap width on analytical data. (a) Autospark controlled gap, (b) AGU controlled gap. $^{39}K^{+1}$ in an ashed biological sample compacted in graphite. All charge accumulations, 0.1 nC.

Magnetic Field Monitor

A magnetic field monitor was constructed which greatly facilitates locating the mass peaks of interest. An inexpensive Hall probe (F. W. Bell, Inc., Model BH206) provides an output voltage analogous to the magnetic field. No significant hysteretic effects are noted, and peak identification is normally to within $\pm$ 0.1 mass unit. The probe is mounted in a non-magnetic shim of 1/16-in Plexiglass (Rohm and Haas) mounted between one magnetic pole and the side of the magnetic analyzer. The probe is outside the vacuum, readily accessible, and well into the magnetic field. Figure 5a shows the position of the probe in relation to the ion flight path. Figure 5b shows the associated equipment needed to construct the field monitor (power supply: Kepco model HB-525; DVM: Heath Universal Digital Instrument Model EU-805). A reference table of mass vs. Hall voltage was compiled for a specific power supply current and ESA voltage.

The precision of the magnetic field monitor is in part due to the placement of the Hall probe well into the magnetic field. To obtain unambiguous mass definition, the probe must be placed in the magnetic field such that it intercepts a flux density truly representative of that which is deflecting the ions. Positioning of the probe outside the analyzer in this study allowed sampling of the field at sequential locations over the magnet pole face in order to determine the most representative flux density, thereby reducing hysteretic effects to a very low level. Referring to Figure 5a, the largest error (poorest reproducibility in locating mass peaks was observed when the probe was placed in position 1. Hysteresis was smaller at position 2, but the measurements were still sufficiently imprecise to preclude positive mass identification. In position 3, hysteresis proved to be quite small, allowing $\pm$0.1 mass unit resolution.

Even with a hysteresis-free probe, accurate peak identification would still not be possible, were it not for very precise measurements of the associated probe parameters. The transverse voltage developed in the Hall probe is governed by the following equation:

$$H_v = k(i \times B) \qquad (1)$$

where H_v is the Hall voltage, k is a constant which includes

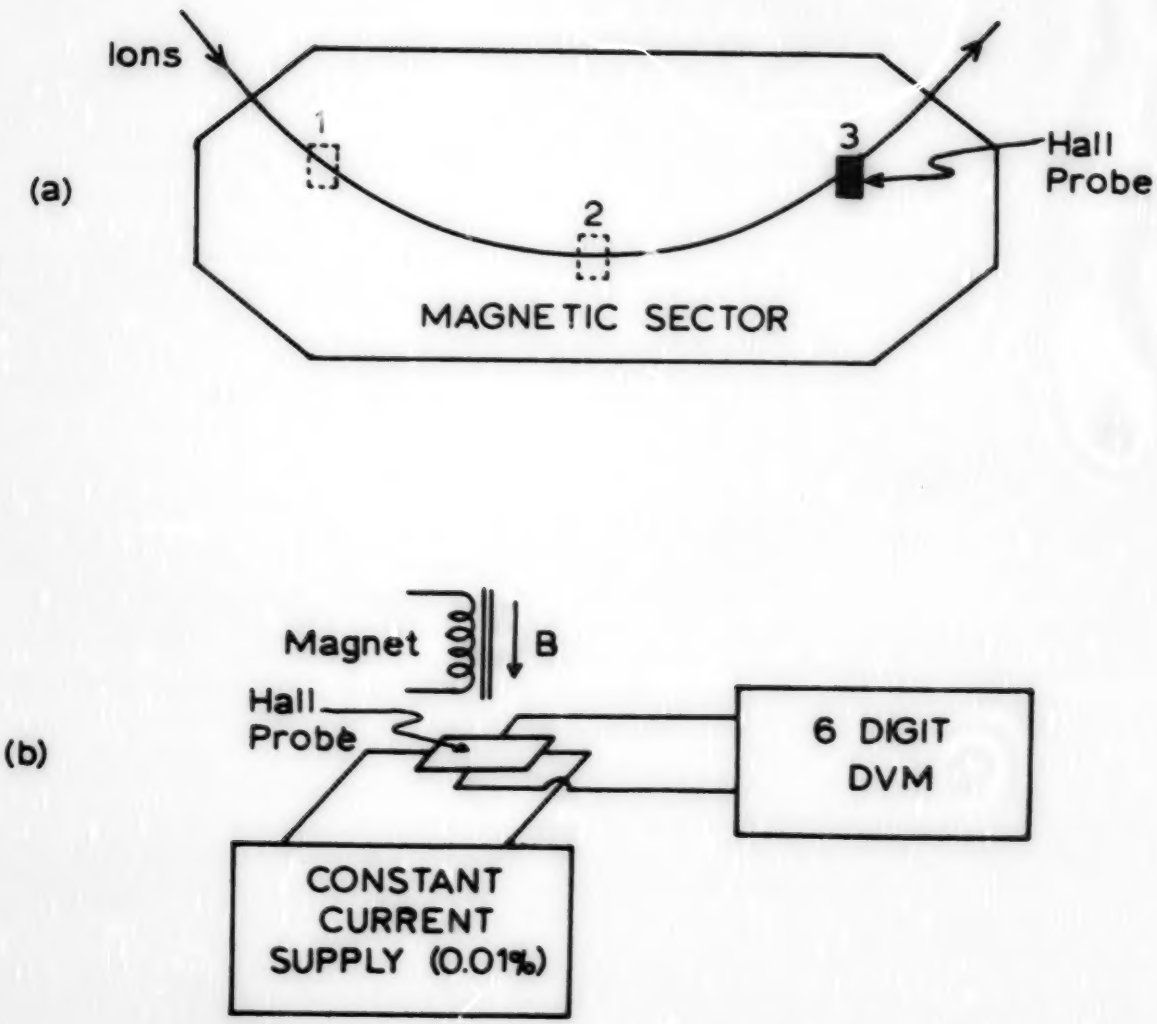

Figure 5. (a) Placement locations of the Hall probe in the magnetic field. (b) Hall probe measurement system (adapted from a drawing of F. W. Bell, Inc., Columbus, Ohio).

geometry, B is the magnetic field strength, and i is the control current, normally considered a vector quantity by nature of its polarity. To obtain a reproducible Hall voltage at a given field strength, the current must be extremely stable. While our supply had good short term (hours) stability of + 0.01%, normal long term drift necessitated measurement (with a six-digit DVM) and subsequent fine adjustment of the current daily. A very accurate measurement and control of the ESA voltage is also necessary to hold the mass-Hall voltage relationship constant. This voltage was also precisely monitored on the DVM and adjusted as necessary. With these precautions, adjustment of the magnetic field to a calibrated Hall voltage can bring a desired mass to register on the collector slit to within ± 0.1 amu. A brief fine tuning of the magnet current by the operator (using the log-ratio for signal maximization) is then usually necessary before peak switch integrations are begun.

Magnetic Peak Switching

The introduction of electrical detection[15,25] to spark source mass spectrometry now allows a significant improvement in precision and accuracy using peak switch integration techniques as compared to photographic detection. Switching from one mass to another can be accomplished by variation of (a) the accelerating and electrostatic analyzer voltages or (b) the magnetic field strength. The former method has been generally used[26,27] because of problems associated with magnet hysteresis. Barton, et al.[28] have shown that magnetic field control is useful for fast sweeps.

Electrostatic peak switching may introduce several problems, including possible changes in ion extraction efficiency, variation of energy band pass into the magnetic analyzer, and electron multiplier gain dependence[29] on ion energy. The general electrostatic peak switch mass limitation of M to 2M before required readjustment of the magnetic field is also a distinct disadvantage when carrying out analysis for many elements.

Magnetic peak switching eliminates these difficulties because the accelerating and ESA voltages remain virtually unchanged. An inexpensive magnet control unit was designed and constructed to allow implementation of magnetic peak switching.

The magnetic Peak Selector (MPS) interfaced to an AEI MS 702 enables the operator to select any ten masses (or more, with add on capabilities) from 6 to 250 amu and bring them onto the collector slit to within $\pm$ 0.1 amu by a switch selected variation of the magnetic field. The unit is comprised of a magnetic field sensing Hall probe interacting with two associated circuits, one a constant current supply to the Hall probe and the other a magnet control system based on the Hall voltage.

The circuit (Figure 6) is built around an operational power supply (KEPCO Model OPS 100-0.2B) furnishing 100 mA to a high sensitivity Hall probe (F. W. Bell, Model BH-206).

Figure 7 shows the control circuit for the MPS. The active elements are an integrating null detector followed by a high voltage driver. When coupled to the Hall probe, these amplifiers form a magnetic feedback loop which drives the magnet to produce a Hall voltage equal to a selected reference voltage, but of opposite polarity.

Internal standard analysis--An advantage of magnetic peak switching is the ability to compare trace constituents with

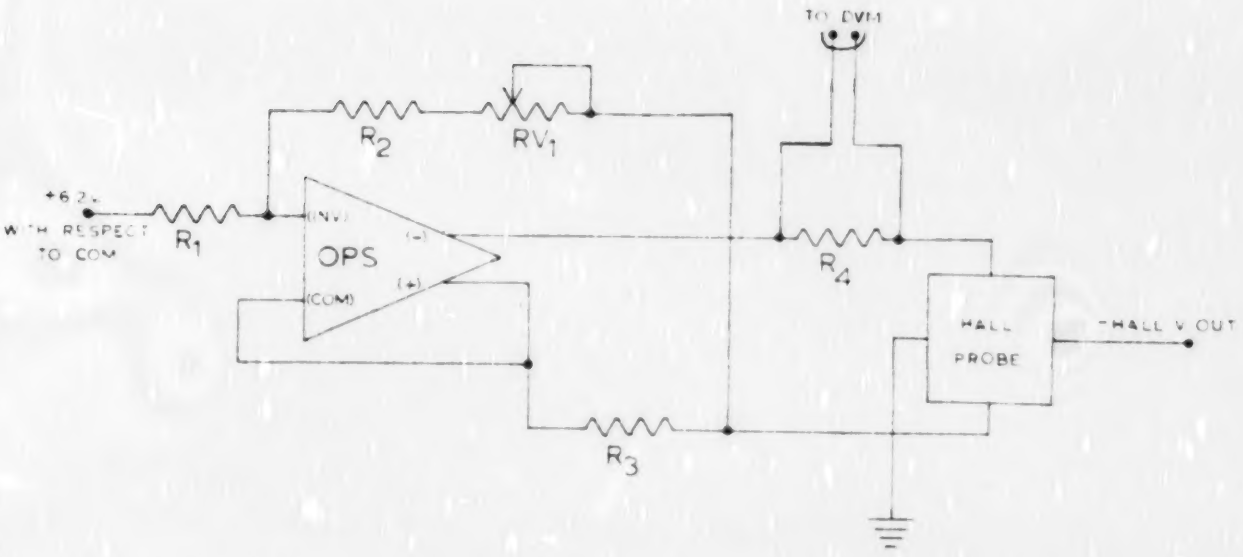

Figure 6. Schematic of MPS Hall probe power supply. See reference 17 for details.

internal standards using high precision integration techniques. Internal standards in SSMS have normally been used only with photographic detection and electrical scanning because for these techniques the accelerating voltage is left unchanged. However, both these procedures suffer from poor precision, ($\sim \pm 30\%$ rel std dev). Electrostatic peak switching shows good precision ($\sim 5\%$ rel std dev), but difficulties arise with the use of internal standards. Sensitivity changes occur, associated with changing the accelerating voltage. Also, a limitation exists in mass of M to 2M without changing the magnetic field. Magnetic peak switching, however, combines the precision of integration techniques with the advantage of a fixed accelerating voltage to allow large numbers of elements to be quickly measured with good accuracy through the use of precise relative sensitivity factors (RSF's). Table 1

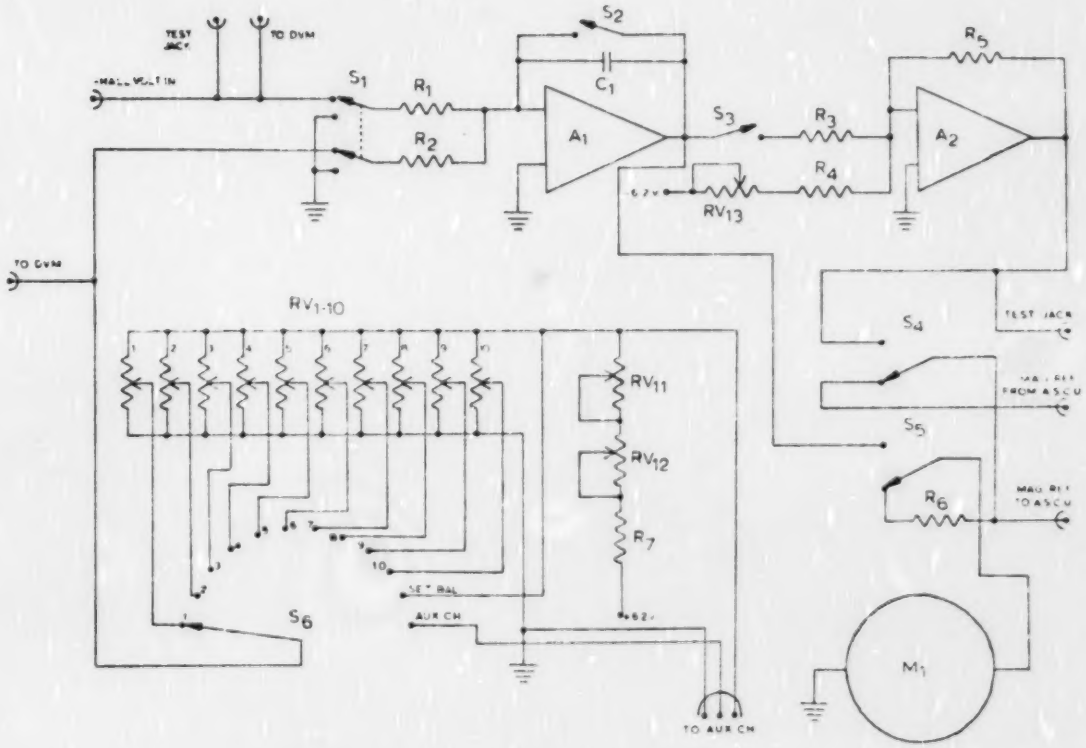

Figure 7. Schematic of MPS control circuit. See Reference 17 for details.

TABLE 1. RELATIVE SENSITIVITY FACTORS[a] AS DETERMINED BY MAGNETIC PEAK SWITCHING

Sample	^{55}Mn	^{56}Fe	^{65}Cu	^{66}Zn	^{75}As	^{80}Se	^{208}Pb
Bovine liver No.1, day 1	2.50	1.56	1.50	1.57	4.60	0.679	1.80
Bovine liver No.1, day 1	2.40	1.57	1.45	1.58	4.81	0.664	1.99
Bovine liver No.1, day 2	2.25	1.42	1.55	1.72	4.28	0.580	1.84
Bovine liver No.2, day 3	2.34	1.57	1.51	1.56	4.85	0.479	2.04
Bovine liver No.1, day 4	2.45	1.56	1.57	1.88	5.32	0.597	2.31

[a]Apparent/true, relative to ^{89}Y.

shows RSFs determined by magnetic peak switching. These data depend not only on the use of the MPS, but also on close monitoring and control of critical experimental parameters, including interelectrode self-shielding and spark-gap . Determination of elemental sensitivities relative to an internal standard using magnetic peak switching has been reported by Hull.[30]

Table 2 shows an example of magnetic peak switching analysis using an internal standard. NBS low alloy steel

TABLE 2. ANALYSIS OF 15 ELEMENTS IN NBS NO. 461 BY MAGNETIC PEAK SWITCHINC SSMS USING A NICKEL INTERNAL STANDARD[a]

Element	Certified, wt%	Found, wt%
C	0.15	0.313
P	0.053	0.047
Ti	(0.01)	0.012
V	0.024	0.021
Cr	0.13	0.187
Mn	0.36	0.429
Co	0.26	0.269
Cu	0.34	0.345
As	0.028	0.030
Zr	(0.005)	0.001
Mn	0.011	0.014
Mo	0.30	0.263
Sn	0.022	0.023
W	0.012	0.011
Pb	(0.003)	0.003

[a] $^{60}Ni^{+1}$ at 0.40 (wt%) internal standard.

No. 462 was used to calculate RSF's for 15 elemental vs. nickel. NBS No. 461 was then analyzed using these RSF's taking five 0.01 nC charge accumulations for each element. The large discrepancy for carbon could not be explained. Chromium and niobium are also less than satisfactory. However, all but four of the elements in Table 2 are close to or within the anticipated 10% accuracy range. RSF's may vary somewhat with matrix. In Table 1 for example, iron shows an RSF of 1.54 vs. yttrium in an electrode of ashed NBS Bovine Liver compacted in graphite. In an electrode of ashed NBS orchard leaves prepared in the same manner, iron shows an RSF of 1.89. The excellent precision ($\sim$ 5%) obtainable with integration methods may be misleading relative to accuracy considerations of a standard and unknown or even to the sample-to sample use of RSF's.

Repetitive Scan Unit

Electrical detection methods in spark source mass spectrometry using both the peak switch and scanning modes have been described.[15] Scanning methods allow qualitative analysis but are generally limited to a precision on the order of $\sim$ 35%.[15] Peak switch techniques can show precision to $\pm$ 5% by careful control of critical parameters[23,31] and at the expense of a considerable increase in analysis time per element. For survey analysis of many elements per sample, time considerations may dictate use of the scanning mode, even given its less satisfactory precision.

Averaging methods have been used to improve spectral signal-to-noise ratios by means of storing and adding repetitive scans. The background noise is random as compared to the unidirectional peak signals, resulting in a net improved spectrum. Such averaging techniques have been applied to mass spectrometry. A small, time-averaging computer has been used with a GC-MS system[32] to permit repetitive scanning and increased sensitivity. Computer controlled multiple scan averaging[33,34] was shown to increase mass measuring accuracy in high resolution spectrometry.

The multichannel analyzer (MCA), a versatile data readout device available in many laboratories, can act as a simple but effective averaging unit for spectra accumulation. The multiscale mode of the MCA has been used to enhance the

measurement precision of isotopic abundances for uranium and plutonium[35] and to determine the isotopic abundance of europium produced by nuclear reactions.[36]

The fluctuating nature of the spark ion source and the poor ion statistics associated with the SSMS scanning mode suggested an opportune use of averaging techniques to enhance the precision of quantitative analysis and improve the attainable elemental detection limits.

Signal averaging has been shown to improve precision and sensitivity in spark source mass spectrometry using manual mass scan repetitions.[15] Described in this report is a versatile asymmetric triangular wave form generator, designed to permit automatic multiple scan accumulations. A range of scan rates is provided by the unit, which in the repetitive mode minimizes operator intervention and error. At fast scan rates, this is particularly important. The repetitive scan unit (RSU) supplies a cyclic sawtooth type magnet reference voltage to a MS-702 spark source mass spectrometer, and can be set to scan all or a selected portion of the full mass range; it also supplies a trigger pulse, which synchronizes the scan of the magnetic field to repetitive spectra accumulation, using the multiscale mode of the MCA. Scan rate and mass region, as well as mass range, are all continuously variable.

The RSU schematic is shown in Figure 8. Operational amplifiers A1, A2, and A3 comprise a triangular waveform generator,[37] modified to produce variable asymmetric triangular waves. A4, is a high voltage operational amplifier which steps up the triangular wave voltage to the required magnitude to drive the magnet reference tube-type circuit. An asymmetric wave allows variable magnet scan times, which may be a few seconds up to several minutes, and also variable magnet reset times to reinitiate the subsequent scan.

CHEMICAL STUDIES

Sediment Samples

The application of SSMS to sediment samples allows a rapid, elemental survey analysis of questioned materials. Inorganic hazards, such as lead, arsenic, and cadmium, could be detected to very low levels. Nonmetals, such as bromine and fluorine, which are not normally analyzed by spectro-

graphic emission or atomic absorption, show good sensitivity by SSMS.

The 14 sediment samples analyzed in this study were obtained from the Environmental Research Laboratory, U.S. EPA, Athens, Georgia. The samples were from a series of sediments, each of which had been previously analyzed by neutron activation analysis, X-ray fluorescence, and spectrographic emission.

Sample Preparation--

The sediment samples, as received at this laboratory, were in various states of dampness. Four (37913, 37914, 37916, and 37919) were visibly wet, appearing as mud. Others (37934 and 37961) were not in mud form but were damp; the particles tended to cling together. The remaining samples were hard and dry, either as lumps or powder. Samples 37936 and 37950 had all the appearances of sand.

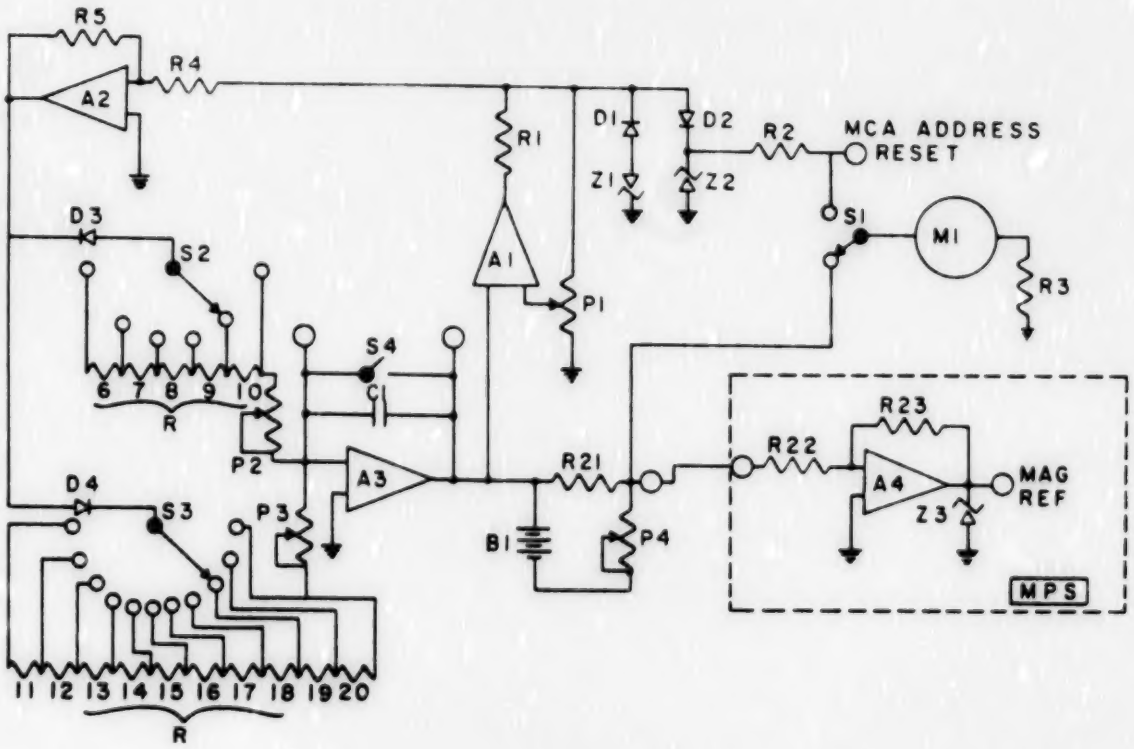

Figure 8. Schematic diagram of repetitive scan unit.

Approximately 1 g of each sample was placed in a 10-ml beaker and broken up, if necessary, with a glass rod. The samples were then transferred to a 100°C oven for 24 hr.

The samples were ashed at 500°C in a muffle furnace for 24 hr to remove any organic constituents.

Table 3 shows the loss upon drying and additional weight loss after ashing the samples. The drying loss values reflect the range of sample conditions from wet to dry and sandy. The ashing loss may indicate organic content of the sediments or water not released at 100°C. The sample showed little or no color change during the drying step, but during the ashing process, many changed in color from brown to light reddish brown. Other portions of these sample which lost the most weight in the high temperature ashing (37913, 37914, 37919) were subsequently ashed in a low-temperature rf asher. A color change from brown to a lighter brown also occured with this ashing.

From each sample that had been high-temperature ashed, 0.200 g was weighed into a 10-ml beaker, and 0.050 g of Ultra-Carbon graphite was added. One milliter of a 10 ppm Y solution (Y_2O_3 dissolved in Suprapur HNO_3 and diluted with distilled deionized water) and 2 drops of ethanol were stirred into the slurry. The samples were then dried in an oven at 100°C, placed in polyethylene vials, along with a plastic ball pestle, and mixed on a Wig-L-Bug for 10 min. Electrodes were prepared from this material by means of an AEI die at 14 tons pressure, using a hydraulic press.

Experimental Conditions--

All data were obtained using an MS-702 spark source mass spectrometer with electrial detection in the log ratio scanning mode.

To enable comparison of results from one sediment to another, the sparking parameters were maintained as constant as possible from sample to sample. The spark gap was set and maintained by Automatic Gap Unit.[22] A gap of 100 μ was used throughout the determinations. Electrode alignment on the ion axis was monitored with a Kennicott telescopic viewing system.[16] Spark voltage was 30 KV, at 300 pulses per second, 100 μsec. pulse length. The distance from the spark to the No. 1 slit was set at 6 mm.

Under these conditions, the ion beam current was about 7% at a ratio-amplifier gain of 10. The flux varied from 5-15%.

The main amplifier gain, as set by the Amplifier and Scan Control Unit (ASCU) was 10, and the electron multiplier settings used were 2.50, 2.85, and 3.50. These settings were experimentally determined to provide the maximum quantitative information, given the concentration of the internal standard. The ratio amplifier time constant was set at 40 ms, and the chart speed on the oscillographic recorder was 0.2 cm/sec. The magnet scan time constant was 200.

Table 3. MOISTURE CONTENT OF SEDIMENT SAMPLES AS MEASURED AFTER HEATING TO 100°C AND ASHING LOSS AFTER HEATING TO 500°C

Sediment sample	%Weight lost at 100°C	%Weight lost at 500°C[a]
37913	61.0	19.2
37914	41.6	13.3
37915	1.15	5.02
37916	39.0	8.32
37919	32.9	12.2
37921	11.5	5.83
37922	3.92	5.92
37923	3.91	4.54
37933	3.08	9.75
37934	21.9	8.40
37936	0.417	1.14
37947	16.8	8.93
37950	1.86	1.28
37961	18.9	7.28

[a]Relative to dry weight.

Data Comparison--

Two scans were taken at each of the 3 multiplier settings. Peak heights were obtained from the scans using a logarithmic scale overlay. For some elements, notably Fe, it was necessary to use an isotope other than the major one. ^{57}Fe was used for all iron determinations. For certain other elements, elemental interferences necessitated the use of small isotopes. ^{71}Ga was used instead of ^{69}Ga due to interference from $^{138}Ba^{+2}$.

The internal standard, Y, was present at a concentration of 10 µg in .250 g or 40 ppmw. At a multiplier setting of 2.50 the Y peak appeared in the middle of the 1st decade on the recorder scale. This was not considered very reliable data and, consequently, the 2.50 scans were seldom used for quantitative results. At a setting of 2.85, the Y appeared at the bottom of the second decade. This set of scans was used to determine the more concentrated elements of interest, including Ti, V, Cr, Mn, Fe, Co, Ni, Rb, Sr, and Ba. At a multiplier setting of 3.50, the elements of lower concentration could be determined; here the Y came to the top of the 3rd decade. Such elements as Pb, Sb, Sn, Cu, Zn, Br, Se, As, and Ga could be detected in the low ppm range.

The data obtained in this manner were used to calculate first the µg of a particular element in the electrodes, and from that the concentration in ppmw in the dry sediment.

In general, two values were obtained for each element in each sample. The micrograms of that element were calculated separately, then averaged for the reported ppm concentration.

The elemental analysis results are reported in Table 4, along with comparison data taken by X-ray fluorescence[38], spectrographic emission,[39] and neutron activation analysis.[40] The INAA values were taken from the 60-minute irradiation values[40] where possible. The spectrographic emission values were taken as the upper limit of the estimated range.[40] In general, the SSMS results agree reasonably well with the other techniques, considering the attendant problems of sample inhomogeneity and variations in both sensitivity and sample handling from one technique to the other. Also, no relative sensitivity factors were used in calculating these results. A unity RSF was assumed for each element relative to the yttrium standard.

Specific elements bear discussion because of their systematic differences from the data offered by other techniques. Fe, for example, is consistently lower than either the X-ray or NAA data. This could be due to a low sensitivity coefficient for iron, brought about by the silicate structure of the sedi-

TABLE 4. COMPARISON OF SSMS ANALYTICAL DATA WITH XRF, FS, AND INAA FOR SEDIMENT SAMPLES (in μg/g)

	No. 37913				No. 37914			
Element	SSMS	XRF	FS	INAA	SSMS	XRF	FS	INAA
Ti	339	—	10K	—	1297	—	10K	—
V	78.5	—	—	54	48.5	—	—	46
Cr	267	—	1K	970	483	—	1K	360
Mn	1858	900	1K	1100	1011	—	1K	410
Fe	34.8K	39K	100K	48K	16.1K	38K	100K	39K
Ni	169	73	1K	—	103	53	1K	—
Co	327	—	—	30	2.78K	—	—	34
Cu	1445	1000	10K	3100	611	1300	10K	1800
Zn	62.5	480	1K	7100	69.3	480	1K	690
Ga	8.05	24	—	—	21.9	26	—	—
As	3280	3000	10K	3300	1530	710	10K	740
Se	10.25	8	—	—	29.3	6	—	—
Br	600	510	—	—	371	420	—	—
Rb	31.8	29	—	—	210	43	—	—
Sr	2240	640	—	—	14.0K	1900	—	—
Sn	29.5	40	10	—	31.4	50	10	—
Sb	117	—	—	73	31.8	—	—	—
Ba	82.3K	27K	100K	48K	343K	77K	100K	90K
Pb	—	410	1K	—	86.0	250	1K	—

TABLF 4. Continued.

Element	No. 37915 SSMS	XRF	FS	INAA	No. 37916 SSMS	XRF	FS	INAA
Ti	5416	4000	10K	—	3239	4700	10K	—
V	119	70	—	32	59.8	160	—	54
Cr	81.3	80	1K	150	187	160	1K	220
Mn	1365	1000	1K	790	437	320	1K	240
Fe	24.1K	32K	100K	41K	20.2K	34K	100K	37K
Ni	100	32	1K	—	121	41	1K	—
Co	33.8	—	—	18	95.5	—	—	18
Cu	19.2	45	1K	470	29.6	83	1K	650
Zn	56.8	180	—	ND	15.4	370	1K	—
Ga	71.2	11	—	—	105	17	—	—
As	7.05	12	—	14	4.53	17	—	16
Se	7.41	4	—	—	10.6	4	—	—
Br	2.93	4	—	—	1.58	12	—	—
Rb	565	63	—	—	256	98	—	—
Sr	248	82	1K	—	479	130	1K	—
Sn	5.9	30	10	—	2.13	30	10	—
Sb	2.45	—	—	1.9	0.63	—	—	2.6
Ba	1207	300	10K	500	2.98K	600	10K	590
Pb	43.2	48	1K	—	16.8	260	1K	—

TABLE 4. Continued.

	No. 37919				No 37921			
Element	SSMS	XRF	FS	INAA	SSMS	XRF	FS	INAA
Ti	2894	2900	10K	—	2305	3900	10K	—
V	786	90	—	36	88.5	130	—	30
Cr	58	590	1K	700	46	240	1K	88
Mn	1395	1000	1K	900	1367	1800	1K	1400
Fe	27K	98K	100K	110K	35.3K	39K	100K	22K
Ni	263	130	1K	—	85.3	11	1K	—
Co	65.3	—	—	16	6.88	—	—	11
Cu	80	230	10K	730	39.3	36	100	300
Zn	18.9	950	1K	1500	25	50	—	ND
Ga	21.2	15	—	—	58.3	17	—	—
As	21.6	10	—	20	—	5	—	2.7
Se	3.08	5	—	—	12.3	7	—	—
Br	9.93	7	—	—	8.25	7	—	—
Rb	70.3	60	—	—	185	75	—	—
Sr	335	260	1K	—	72.3	39	1K	—
Sn	79.8	70	10	—	15.8	50	10	—
Sb	1.52	—	—	47	15.2	—	—	.91
Ba	543	500	10K	1000	250	400	10K	430
Pb	20.4	320	1K	—	—	30	100	—

TABLE 4. Continued

Element	No. 37922 SSMS	XRF	FS	INAA	No. 37923 SSMS	XRF	FS	INAA
Ti	7494	7400	10K	—	2885	5400	10K	—
V	167	190	1K	76	58.5	130	—	59
Cr	178	130	1K	130	211	100	1K	80
Mn	155	150	1K	160	693	1100	1K	820
Fe	47.8K	36K	100K	34K	20.9K	32K	100K	25K
Ni	198	14	1K	—	115	14	1K	—
Co	44.8	—	—	15	15.3	—	—	10
Cu	9.13	45	100	360	61.5	29	100	550
Zn	6.68	93	—	ND	40	85	—	ND
Ga	5.65	20	—	—	83.8	13	—	—
As	10.9	13	—	14	6.83	6	—	6.1
Se	—	4	—	—	3.55	4	—	—
Br	—	8	—	—	—	4	—	—
Rb	27	68	—	—	321	76	—	—
Sr	46.8	57	1K	—	415	77	1K	—
Sn	457	30	10	—	14.5	30	10	—
Sb	—	—	—	0.37	2.7	—	—	.81
Ba	1481	300	10K	370	723	500	10K	390
Pb	—	51	100	—	6.95	28	100	—

TABLE 4. Continued.

	No. 37933				No. 37934			
Element	SSMS	XRF	ES	INAA	SSMS	XRF	ES	INAA
Ti	1203	7300	10K	—	2361	4400	10K	—
V	72.8	200	—	86	123	150	—	79
Cr	231	190	1K	260	268	80	1K	45
Mn	335	1000	1K	1400	345	220	1K	390
Fe	21.4K	52K	100K	58K	25.3K	30K	100K	34K
Ni	153	52	1K	—	29.9	16	1K	—
Co	20.5	—	—	35	29.8	—	—	12
Cu	182	112	10K	1000	51.5	27	1K	650
Zn	2.93	370	1K	ND	119	56	1K	ND
Ga	36.5	25	—	—	356	17	—	—
As	7.98	6	—	13	21.8	7	—	13
Se	2.83	4	—	—	3.63	4	—	—
Br	3.6	7	—	—	12.3	21	—	—
Rb	249	130	—	—	811	64	—	—
Sr	211	100	1K	—	780	100	1K	—
Sn	8.6	50	10	—	5.95	30	10	—
Sb	4.55	—	—	1.7	4.23	—	—	.52
Ba	180	700	10K	1600	1075	200	10K	560
Pb	—	110	1K	—	24.6	32	1K	—

TABLE 4. Continued.

Element	No. 37936 SSMS	XRF	ES	INAA	No. 37947 SSMS	XRF	FS	INAA
Ti	4463	—	10K	—	5016	4500	100K	—
V	189	—	—	17	131	150	100	73
Cr	192	NA	—	26	471	80	10K	150
Mn	858	—	1K	420	1431	630	10K	400
Fe	69.5K	—	100K	84K	130K	42K	100K	45K
Ni	323	—	—	—	358	39	1K	—
Co	23.2	—	—	3.7	66	—	100	20
Cu	6.63	NA	100	310	70.3	62	10K	2200
Zn	3.38	—	—	—	34.5	130	—	—
Ga	21.2	—	—	—	69	16	—	—
As	1.89	—	—	5	11.6	7	—	12
Se	—	—	—	—	2.85	4	—	—
Br	.963	NA	—	—	13.7	110	—	—
Rb	242	—	—	—	187	59	—	—
Sr	164	—	1K	—	523	260	1K	—
Sn	4.8	—	—	—	7.23	30	10	—
Sb	—	—	—	.46	—	—	—	—
Ba	494	NA	10K	260	1563	600	10K	570
Pb	5.8	—	100	—	—	51	10	—

TABLE 4. Continued.

	No. 37950				No. 37961			
Element	SSMS	XRF	FS	INAA	SSMS	XRF	ES	INAA
Ti	6602	3600	100K	—	6300	4000	100K	—
V	161	60	100	39	91	50	100	63
Cr	230	340	100	550	273	80	10K	110
Mn	1376	390	100K	490	1084	400	10K	400
Fe	28.9K	18K	100K	18K	28.7K	35K	100K	35K
Ni	138	9	100	—	231	21	1K	—
Co	775	—	100	6.9	181	—	100	7.8
Cu	31.8	14	1K	2200	78.3	36	10K	2100
Zn	36	35	—	ND	73.5	79	—	—
Ga	62.3	13	—	—	89	17	—	—
As	61.8	5	—	4.8	189	6	—	7
Se	3.53	4	—	—	—	4	—	—
Br	18.0	10	—	—	40.3	56	—	—
Rb	709	61	—	—	209	88	—	—
Sr	1452	390	1K	—	2521	400	1K	—
Sn	18.3	40	100	—	4.6	20	10	—
Sb	13.9	—	—	1.01	—	—	—	1.2
Ba	3400	700	10K	1300	2.75K	1300	10K	1800
Pb	22.9	27	10	—	—	22	10	

ments. Also, a large difference in concentration exists between the iron and yttrium. Even though the ^{57}Fe isotope was used, the yttrium peak was generally quite low in those scans which were of sufficiently low sensitivity to keep the ^{57}Fe peak on scale.

Pb was another problem element, in that it was difficult to verify and measure the lead peaks in several (six) of the samples. In all six of these samples, X-ray fluorescence found over 10 ppm of Pb, well within the routine detection limits of SSMS at the gains used. Pb is, however, less sensitive on a weight basis than lighter elements due to the ppma-ppmw relationship and the mass dependence of the electron multiplier response.

In this study, lead was not reported unless the pattern of the 208-207-206 isotopes was clear. The 208 peak was used for calculations. If this pattern was not present in a reasonably accurate distribution in the scans, no lead data were taken. This was done to preclude the use of spurious peaks.

There is a possibility that some Pb was lost from the samples during the high temperature ashing stage, in the case of sample 37913, which showed the highest Pb by X-ray fluorescence, but no detectable Pb by SSMS, further scans were taken at a higher gain. These did reveal lead peaks, but at a level down from the X-ray and spectrographic emission data by a factor of 10. In other work done at this laboratory, Pb was deposited as the nitrate from solution onto graphite, and no significant Pb loss was observed. However, due to the nature of the Pb in sediment type samples, some loss may have occurred at 500°C.

Ni was consistently higher (by a factor of 2) by SSMS than by X-ray fluorescence. This may be explained by a higher sensitivity factor or by molecular interference. The most probable interferents in these samples would be silicon containing species, e.g., Si_2, SiO, SiO_2. Silicon has 3 isotopes, thereby providing 6 possible Si_2 masses, notably 56, 57, 58, and 59. All of these masses were used in this study to determine, respectively, Fe, Ni, and Co. Ni^{60} was not used because of the possibility of C_5 and SiO_2 species interference. Some measure of the possible interference on masses, 57 and 59 can be gained by comparison to the +2 lines. The molecular interferences do not normally doubly ionize.

The Rb and Sr values are also higher than the X-ray data. There are possible interferents occurring at masses 85 and 88, such as FeSi and FeO_2. The nature of molecular interferent formation makes it difficult to predict which of the many possible species will be large enough to significantly alter the data.

The above discussion has pointed out individual elements and the problems involved in their determination. The type of sample presented by these sediments is a subject for a more general discussion. The accuracy and precision of the data depend to a large extent on the physical and chemical nature of the electrodes.

Perhaps the greatest concern in handling the sediments is homogeneity. As they were received, the samples appeared to have gross inhomogeneities. The sandy samples showed grains of various colors and textures. Other samples were in lumps of various sizes and degrees of wetness. After drying and crushing, many of the samples took on a more even color and texture. The particle size was still rather large, but only 3 or 4 samples (37915, -21, -36, and -50) showed gross inhomogeneity at this point.

The samples were vibrated in a Wig-L-Bug after mixing with carbon and deposition of the Y solution. Although the plastic vial and ball pestle are not hard enough to grind silicate material, friction and impact of the particles with each other should cause some reduction in size. One sample (37936) required grinding in an agate mortar and pestle to powder it prior to use of the Wig-L-Bug. Particle size, and the behavior of these particles in the spark discharge may significantly affect the analytical data. Homogeneity of the sample and a consistent electrode surface geometry are extremely important for best SSMS results.

SSMS has been shown to be an acceptable survey trace analysis technique for bottom sediment samples. Using log ratio scanning, a large amount of data can be rapidly taken. Agreement of this data with other analytical techniques is generally good, provided care is taken to standardize and control experimental parameters.

Sample preparation is important in that the particle size of some sediments may require reduction for best analytical re-

sults. The use of two internal standards might also be considered if all elemental constituents, majors to trace, are to be analyzed. Alternatively, a multi-isotope standard element could be employed. For elements of particular interest, where greater analytical precision and accuracy may be desired, peak switch integration techniques may be used.

Biological Samples

The electrical nature of the spark-source requires that the sample electrodes be electrically conducting in order for the discharge and subsequent ionization to occur. Biological compounds such as hair, nails, and tissue must be treated in such a way that they can be made to conduct, or, rather, be placed in a conducting sample matrix. Even if hair or nails could be made to spark directly in their natural state, serious problems would still result which would require sample pretreatment. The organic constituents in the biological samples produce an exceedingly complex spectrum which would make identification and quantitation of the inorganic constituents virtually impossible. Therefore they must be removed by one of the ashing procedures.

In principle the ashed samples may be mixed with any good conductor. However, there are certain practical considerations that dictate matrix peoperties.

(1) Purity. The matrix should be of the purest grade possible. Since the bulk of the electrode will be made from this material; purity requirements are stringent. Grades known as "spectrographically pure" are often not satisfactory. High-purity silver and gold are often used, but their trace element concentration may be unacceptable, depending on the manufacturer. A special grade of graphites is now available which seems to be very low in impurities and consistent from batch to batch.

(2) Physical Nature. Only a small amount of each electrode, perhaps 1 mg, is consumed during the analysis. This puts severe homogeneity requirements on the sample ash-matrix mixture. Many metal powders are too coarse to allow the proper intimate mixing of the ash and matrix. Again, the graphite is much better in this respect because the Ultra Superior Purity grade 1-M is extremely finely divided (< 1 μm mesh) and provides an excellent homogenization character.

(3) Chemical Nature. An ideal matrix might be monoisotopic, low atomic weight, with no tendency to form polyatomic species or molecular units with sample elements. A monoisotopic matrix removes fewer mass lines from analytical use, the low atomic weight reduces interference from multiply charged matrix ions, and the tendency to maintain the atomic ionic state also reduces interferences. No matrix meets all these requirements, of course. Graphite interferences are not usually severe and are centered around the polycarbon lines which must generally be avoided. Selection of proper spark conditions can reduce molecular species.

Sample Ashing--

There are three "standard" approaches to tissue ashing (or oxidation) along with many more specialized methods. High temperature dry ashing (HTDA) involves simply heating the dried tissue in a furnace to some suitable temperature, perhaps 500- to 600°C, to remove by oxidation the organic constituents. The method is simple, effective, and relatively inexpensive. Some inorganics, such as mercury, may also be volatilized, however. Furthermore, the alkali salts of a tissue may form a hard glossy residue which is difficult to remove from the ashing container. In the case of quartz ashing boats, the salts will attack the surface and soon ruin the boat. Low temperature dry ashing (LTDA) uses an rf discharge to produce atomic oxygen which then reacts with dried tissue at relatively low temperatures. It is slower than HTDA, but the lower temperature may be useful to prevent volatilization. For tissues, perhaps a larger advantage is the physical nature of the ashed sample; an easily handled powder ash results. Wet ashing[41] relies on the use of oxidizing acids, such as HNO_3, and $HClO_4$, to oxidize in solution the organic components of the tissue. Low temperatures ($\sim 200°C$) can be used. For techniques which use solution samples, notably atomic absorption, wet ashing is a very convenient method, although the analyst must develop familiarity with specific acids and their rates of reaction under controlled conditions. $HClO_4$ digestions can create unstable situations for the novice. However, a mixture of HNO_3 and $HClO_4$ can be used quite safely and efficiently if properly monitored.[42]

Each of these ashing methods can produce a sample suitable

for SSMS analysis. The experienced analyst may exhibit a preference for a particular method because of past usage, but in proper hands, each can be successful. We have used all three methods in our laboratory and prefer the LTDA approach. However, each technique has weaknesses that must be considered. See the EXPERIMENTAL of this report for descriptions of the ashing procedures. The use of these or similar procedures has been reported for the analysis by SSMS of tissues[43] and hair[14].

Although LTDA is slower and less amenable to large numbers of samples, we prefer it for the following reasons:

1. An easily handled ash residue is produced
2. The low temperatures minimize elemental volatilization
3. The clean oxygen environment minimizes pick up during ashing.
4. No addition of liquid reagents (as in wet ashing) is necessary.
5. The residue is in a form that readily combines with graphite for SSMS analysis.

SECTION V

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